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(54) Dental material usable as E.g. fissure sealant

(57) Composite resin for dental use (such as fissure sealant or for a denture) or orthopaedic cement, made from chemically- or radiation- cured resin is filled e.g. with mica. Other possible fillers are in the form of fibres or flat plates, and include talc, laponite, zeolite, kaolinite and/or vermiculite.

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DENTAL MATERIAL USABLE AS E.G. FISSURE SEALANT

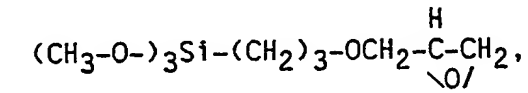
This invention relates to a dental material usable in bulk for dentures or as a restorative such as for a fissure sealant for use in producing coatings on dental enamel, to a process for coating dental enamel, to a method for cosmetic colouring of teeth using the sealant and to a method for prophylactic protection of teeth using the sealant. The material may also be used as an orthopaedic cement.

Fissure sealants have been demonstrated as effective in reducing incidence of tooth decay and inhibiting decay even after it has started, but have not gained widespread acceptance in general practice. These fissure sealants are understood to be somewhat soft, adhering to the tooth with a rather short half-life (5 years).

Both light-(e.g. blue-violet (450-470nm))-cured and chemically cured resins are commercially available. A typical light-cured dental fissure sealant comprises approximately 44% by weight bis-phenol A-glycidyl methacrylate resin adduct (bis-GMA), 48% triethylene glycol dimethacrylate, traces of light initiators, 1% ground titanium dioxide and 6% colloidal silica. A typical chemically cured dental fissure sealant is a two-pack product, mixed immediately before application, where the first pack is similar to the light-cured sealant described but with the light initiators replaced by cross-linking assistants, and where the second pack consists of 51% bis-GMA, 47% triethylene glycol dimethacrylate and the balance cross-linking initiators.

According to the invention, an orthopaedic cement or dental material such as a denture or fissure sealant composition comprises a chemically or radiation-curable resin with optionally a thinning solvent (alcoholic or non-alcoholic) and with a filler, characterised in that the filler is in the form of fibres or flat plates, such as talc or mica, or laponite,

zeolite, kaolinite or vermiculite or a mixture, optionally coated (preferably by chemical vapour deposition) with for example titanium dioxide, chromium oxide or ferric oxide or a mixture, the filler preferably comprising up to 70%, e.g. up to 50%, e.g. up to 30% by weight of the composition. Other coating methods can be used alternatively or in addition, such as deposition of silane. This can promote and enhance mechanical properties. As silanising agents, compounds containing a glycidoxy group and a polyalkoxy e.g. trimethoxy silyl group may be used, such as



for example Dow Corning Z6040 (trade mark). The filler may comprise from 0.1% by weight (for a cosmetic effect) and in preferred cases ½ to 5% such as around 1%. For a mechanical effect too, there may be up to 10 or even 30% filler. The filler may additionally comprise other additives such as TiO_2. Also according to the invention, an orthopaedic cement or dental material such as a denture or coated composition comprises a cured resin containing a filler as set forth above. Such filler materials are harmless if swallowed in the small quantities in which they might spall off. The filler particles' aspect ratio is preferably at least 5:1. The mean filler particle size is preferably up to 3μm (e.g. 0.1 to 2μm) in one dimension and 5-100μm in the other two dimensions. Where the latter dimensions are 5-20μm, the filler preferably comprises from 20 to 30% by weight of the composition, and where those dimensions are 10-60μm, the filler preferably comprises 10-20% by weight of the composition. On the other hand, it has also been found that smaller particles can be present in smaller weight proportions. Cross-laid fibres may be used. In the case of an aerated resin, say one which is 90 volume % air, a platey filler will improve its mechanical properties such that it could be used as an insulating material, or the cavities can be used as drug reservoirs, which will slowly release, on a tooth or otherwise.

The filler improves bending fatigue somewhat and hardness more substantially, and reduces the incidence of crazing in the cured resin (not only in dental applications) by physically reducing the bulk of resin needed, thus making what there is of it more elastic. It can improve the adaptation (i.e. conformation) of the resin onto the tooth surface. It can also absorb incident light or laser energy and (by reflection) re-emit it to the resin, in favourable cases accelerating the latter's curing. The filler also improves the abrasion resistance of the cured resin coating, which is thus less likely to be worn or chipped away. The filler may be a major component of the product. In the case of mica, which tends to fall out of suspension quite rapidly, it may be advisable to incorporate it into the resin when the latter is made up, possibly with stabilising agents; as the resin polymerises, the polymers grow on the mica, improving its suspension and bonding. On the other hand, a too-perfect suspension is to be avoided; as it is, the mica advantageously settles into pits and fissures, whither it is drawn by surface tension. This inhibits crack propagation by increasing the path length of any crack from the air suface to the tooth surface. Further advantages of mica in relation to dentures and orthopaedic cements are its possible radio-opacity and its toughening effect against fatigue. Its radio-opacity may be useful in identifying cement where repeated interventions are indicated, and in the case of dentures, radio-opacity may help prevent instances of patients choking on unidentified objects, namely X-ray-transparent dentures which they have swallowed.

The solvent is preferably an alcohol and is present in a proportion of preferably 1 to 99, e.g. 40 to 60 volume %, the viscosity of the solution is preferably 1 to 10 poise, e.g. 5 to 8 poise.

A method for cosmetic colouring of a tooth according to the invention comprises applying a material as set forth above to a tooth and curing the material. The tooth may have been treated with restorative material such as glass alkenoate cement, for

which the present invention can be regarded as providing a varnish. The resin may include a pigment. Alternatively, the filler itself is so formulated as to appear a tooth-like colour in the applied thickness. Alternatively, the tooth is stained cosmetically, and the stain retained by the applied coating. As a side-effect, prophylactic benefits may be obtained.

A method for prophylactic protection of a tooth according to the invention comprises applying a material as set forth above to a tooth and curing the material. The tooth may have been treated with restorative material such as glass alkenoate cement, for which the present invention can be regarded as providing a varnish. Preferably the filler is so formulated as to appear a tooth-like colour in the applied thickness. (The coating thickness and/or proportion of filler can themselves alter the colour.) As a side-effect in that case, cosmetic benefits may be obtained.

Preferably the tooth is cleaned beforehand e.g. mechanically or by acid-etching.

The present invention provides a method of slow drug release, comprising allowing a coating produced by resin as set forth above and charged with the drug to ablate.

The resin coating is vulnerable to cracking during curing as density increases mainly in the vertical direction and not the horizontal. Thin coatings that are less than ¼μm generally do not suffer from cracking and have better mechanical durability.

Using liquid spreading techniques likely to be available in ordinary clinical practice, even using diluted resin, would however yield coatings on tooth surfaces having a thickness of approximately 5-10μm. The addition of inert fillers such as mica flakes permits even coatings of this thickness to cure crack-free.

These coatings may be applied to:-

(i) Fissure sealing

(ii) Sealing marginal gaps arising from old restorations

(iii) Entire tooth crown surface protection

(iv) Root canal therapy, e.g. sealing tubules

(v) Lining freshly prepared cavities (blocking open tubules)

(vi) Protection of cavities freshly restored with glass ionomer/composite surfaces

(vii) Replacing porcelain veneers for aesthetically discoloured enamel surfaces

coating

(viii) Slow release of fluoride for topical application to tooth, and

(ix) Controlled release of drugs for example in the treatment of dentine hypersensitivity or periodontal disease.

The invention will now be described by way of example.

Two multicomponent resins were prepared.

Example 1: light-cured

Example 2: chemically cured

The light-cured resin of Example 1, before fibrous or platey fillers according to the invention are taken into account, comprised by weight:-

44.32% bis-phenol glycidyl methacrylate resin adduct

48.14% triethylene glycol dimethacrylate with inhibitor

0.45% dimethylaminophenethanol

0.22% camphorquinone

0.87% titanium dioxide (ground to <4μm)

6.00% colloidal silica

The chemically cured resin of Example 2, before fibrous or platey fillers according to the invention are taken into account, comprised two packs, to be mixed 1:1 by weight (whereupon chemical curing would take place). These packs, before fibrous or platey fillers are taken into account, comprised by weight:-

Pack 1: 41.94% bis-phenol glycidyl methacrylate resin adduct

46.29% triethylene glycol dimethacrylate with p-methoxy phenol inhibitor

1.99% dihydroxy p-toluidine

0.92% 2(2'-hydroxy 5'-methylphenyl)benzotriazole
0.73% phenylsalicylate-glycidyl methacrylate adduct
0.13% triphenyl stibine
1.96% titanium dioxide ground to <4μm
6.04% colloidal silica

Pack 2: 51.42% bis-phenyl glycidyl methacrylate resin adduct
46.58% triethylene glycol dimethacrylate with inhibitor
1.13% benzoyl peroxide
0.80% phenylsalicylate-glycidyl methacrylate adduct
0.07% butylated hydroxytoluene

The resins of Examples 1 and 2 contain inert fillers according to the invention. Inert fillers such as "ceramic colours" of particle size 2-10μm (1-5 weight % additional to the resin, taken as 100%) were used but tended to settle out of the uncured resin with time. Small particles of mica were successfully loaded and greatly improved the quality of the coating and its mechanical properties.

The mica, in plates 1-2μm thick and 10-50μm in the other two dimensions, was fully coated with a Fe_2O_3/TiO_2 mixture, which controlled the colour and is believed to have assisted bonding with the resin (which itself bonds chemically to natural tooth). It was found that the mica plates lay in place well, parallel to and adapting to the tooth surface.

In the case of Example 2, mica was incorporated in either or both packs. Satisfactory curing was achieved with all micas. In the case of Example 1, translucent mica (i.e. the third TiO_2 in the following table) worked well, refracting incident light throughout the resin. White mica (i.e. all other TiO_2 in the table) also worked well, because strong reflections off the platelets bounced all round inside the bulk and cured it. The thickness of the TiO_2 affects the shade, and can be adjusted as required. Coloured opaque mica (the Fe_2O_3 in the table) was less satisfactory in Example 1, because radiation energy could not penetrate sufficiently into the deeper layers. The coated micas used were:-

Particle size	Coating Type	Appearance	% used by weight total	Coating Quality
10-60μm	TiO_2 (Anatase)	Silver pearl	15	Good
10-60μm	TiO_2 (Rutile)	Silvery	15	Good
2-20μm	TiO_2 (Anatase)	Lustre satin	30	Good
40-200μm	TiO_2 (Anatase)	Flash pearl	10	Poor
40-200μm	TiO_2 (Anatase)	Shimmer pearl	10	Poor
10-60μm	TiO_2 (Rutile)	Lilac pearl	15	Good
10-60μm	Fe_2O_3	Royal Gold	15	Good
10-60μm	Fe_2O_3	Bronze	15	Good
10-60μm	Fe_2O_3	Red	15	Good

Mica is a naturally occurring alumino-silicate ($KAl_2(AlSi_3O_{10})OH$). Its surface even in the uncoated state is thought to become chemically bonded to the resin. Only a very thin covering of resin is present over and in between the mica plates, and this reduces the tendency of the cured resin coating to suffer from stress-relief cracking.

The physical properties of mica, that is good thermal and electrical insulation, high mechanical resistance, and low coefficient of friction, may also contribute to the lack of resin cracking. Furthermore, the mica plates or flakes are oriented parallel to the surface on which the thickness of the coating has been applied, and this will arrest crack propagation normal to the surface, since such a crack must suffer lengthy 'detours' around the mica plates i.e. fracture length has been greatly increased.

The resins were applied to a recently extracted acid-etched human molar tooth via an analogous method to dip-coating. One to three drops (approximately 100-300μl) of the diluted resin solution were deposited on to the tooth surface, a single drop

sufficing for the whole occlusal surface. The liquid was spread over the surface with a jet of compressed air or a chip syringe. This simple method generated a thin coat of liquid. Compressed air thinning serves three important functions:

(i) Resin was forced into small crevices, pits and fissures

(ii) Excess resin is removed leaving a very thin film of liquid on the surface

Typically, the applied dry-weight resin loading over the surface was 7-13mg/mm^2, equivalent to a consolidated coating thickness of the order of 10^1 mm.

The coatings according to all versions of the Examples had exceptional aesthetic qualities, and a very wide range of colours and shades of white is available. Note that mica and particulate materials such as titanium dioxide may be used in combination.

Example 2 was repeated in five trials, to establish the effect of the filler on abrasion resistance. The filler was TiO_2-coated mica in each case. In each Trial, samples were made up (11-12mm diameter and 1.1mm thick on a clean glass slide) using the chemically curable resin fissure sealant. The total mass of material tested had a range of 150-22mg. These materials were stored in water for at least 24 hours prior to testing. The surfaces were abraded for 90 minutes using a brushing machine (total number of brush strokes (bi-directional) 178-182 per minute). A new toothbrush was used for each specimen with a constant load of 360g. Conventional dental pumice (an aggressive abrasive) was used in the form of a 50% wt/vol slurry in distilled water. The weight loss was measured after 90 minutes of abrasion. Intermediate durations showed a roughly linear rate of abrasion.

Trial 1 was a control, conducted on the fissure sealant with no filler.

In Trials 2-5, according to the invention, the filler was:-

Trial 2: 10% wt/wt TiO_2 (anatase)-coated mica, plates 10-60μm

Trial 3: 10% wt/wt TiO_2 (anatase)-coated mica, coloured flash pearl, plates 40-200μm

Trial 4: 15% wt/wt TiO_2 (anatase)-coated mica, coloured shimmer pearl, plates 40-200μm

Trial 5: as Trial 1, the mica being silanised with Z-6040 before having been TiO_2-coated.

Results:-

Trial 1: % weight loss of coating:
Mean = 54%, Standard Deviation = 5.4% n = 5

Trial 2: % weight loss of coating:
Mean = 61%, Standard Deviation = 3.8% n = 5

Trial 3: % weight loss of coating:
Mean = 61½%, Standard Deviation = 8.7% n = 6

Trial 4: % weight loss of coating:
Mean = 59%, Standard Deviation = 7.1%, n = 5

Trial 5: % weight loss of coating:
Mean = 67%, Standard Deviation = 2.0%, n = 6

Thus it can be seen that the presence of mica appears to increase the abrasion resistance of resins by 10-20%.

Example 3: A two-pack (solid + liquid) chemical curing denture acrylic (How medica Simplex Rapid, trade mark) was made into cuboidal specimens 5mm x 10mm x 60mm for Vickers hardness testing. The comparative specimens were unfilled, and specimens according to the invention contained 10 weight % anatase-coated mica of 10-60μm particle size.

Comparative A (2.5 solids = 1 liquid):
Hardness = 15.9
Standard Deviation = 2.7 (26 trials)

Comparative B (1.7 solids: 1 liquid):
Hardness = 16.4
Standard Deviation = 0.4 (12 trials)

Invention (2.5 solids: 1 liquid, which, allowing for the mica, equates to 1.7 polymer : 1 liquid):
Hardness = 19.5
Standard Deviation = 2.4 (25 trials)

CLAIMS

1. An orthopaedic cement or dental material, comprising a chemically or radiation-curable resin and a filler, characterised in that the filler is in the form of fibres or flat plates.

2. A cement or material according to Claim 1, wherein the filler is talc, mica, laponite, zeolite, kaolinite, vermiculite or a mixture.

3. A cement or material according to Claim 1 or 2, wherein the filler is coated.

4. A cement or mixture according to Claim 3, wherein the filler is coated by chemical vapour deposition.

5. A cement or mixture according to Claim 3 or 4, wherein the filler is coated with titanium dioxide, chromium oxide or ferric oxide or a mixture thereof.

6. A cement or mixture according to any preceding claim, wherein the filler comprises up to 70% by weight of the composition.

7. A cement or mixture according to Claim 6 wherein the filler comprises up to 50% by weight of the composition.

8. A cement or mixture according to Claim 6 wherein the filler comprises up to 30% by weight of the composition.

9. A cement or mixture according to Claim 6 wherein the filler comprises up to 5% by weight of the composition.

10. A cement or mixture according to any preceding claim, wherein the filler comprises from 0.1% by weight of the composition.

11. A cement or mixture according to any Claim 10 wherein the filler comprises from ½% by weight of the composition.

12. A cement or mixture according to any preceding claim, further comprising other additives.

13. A cement or mixture according to Claim 12, wherein said other additives comprise titanium dioxide.

14. A cement or mixture according to any preceding claim, wherein the filler particles' aspect ratio is at least 5:1.

15. A cement or mixture according to any preceding claim, wherein the mean filler particle size is up to 3μm in one dimension and 5-100μm in the other two dimensions.

16. A method for cosmetic colouring of a tooth, comprising applying a material according to any preceding claim to a tooth and curing the material.

17. A method for prophylactic protection of a tooth, comprising applying a material according to any of Claims 1 to 15 to a tooth and curing the material.

18. A method of slow drug release comprising allowing a coating of resin charged with a drug and produced by a method according to Claim 17 to ablate.

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E miner's report to the Comptroller under Section 17 (The Search Report)

Application number
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Relevant Technical fields

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(ii) Int Cl (Edition 5) A61K, A61L

Search Examiner
M J PRICE

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Databases (see over)

(i) UK Patent Office

(ii) WPI

Documents considered relevant following a search in respect of claims 1-15

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2086398 (KULZER) the whole document	1-15
X	GB 1419640 (IEE) the whole document	1-15
X	GB 1414678 (COLGATE) the whole document	1-15
X	GB 1129525 (3M) the whole document	1-15
X	WO 90/08799 (HALL) the whole document, eg Claim 9	1-15
X	US 4141144 (LUSTGARTEN) the whole document	1-15
X	US 4107845 (LEE) the whole document	1-15
X	US 3944661 (COLGATE) the whole document	1-15
X	JP 63077807 (UNITIKA) see WPI Accession number 88-136313/20	1-15
X	JP 58079911 (SANKIN) see WPI Accession number 83-59969K/25	1-15

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

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